



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Enhanced bioelectricity generation by double-chamber air-cathode catalyst-free microbial fuel cells with addition of non-consumptive vanadium (V)

Citation for published version:

Borthwick, A, Li, J, Zhang, B & Song, Q 2016, 'Enhanced bioelectricity generation by double-chamber air-cathode catalyst-free microbial fuel cells with addition of non-consumptive vanadium (V)', *RSC Advances*, vol. 2016, no. 39, pp. 32940-32946. <https://doi.org/10.1039/C6RA01854H>

Digital Object Identifier (DOI):

[10.1039/C6RA01854H](https://doi.org/10.1039/C6RA01854H)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

RSC Advances

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Cite this: *RSC Adv.*, 2016, 6, 32940

Enhanced bioelectricity generation of double-chamber air-cathode catalyst free microbial fuel cells with the addition of non-consumptive vanadium(v)

Jiaxin Li,^a Baogang Zhang,^{*a} Qinan Song^a and Alistair G. L. Borthwick^b

Improvement of microbial fuel cells (MFCs) *via* bioelectricity recovery is urgently needed in micro-energy devices nowadays. Herein, we demonstrate that the power outputs of double-chamber air-cathode catalyst free MFCs can be increased by approximately 40% through the cyclical redox of vanadium (between v and iv) in the catholyte. The enhanced performance can be explained by the regenerated vanadium(v) resulting from aeration of residual vanadium(iv) on the cathode surface as well as an accelerated electron transfer rate in the aqueous solution. This study provides a simple and cost-efficient strategy to improve the performance of MFCs.

Received 21st January 2016
Accepted 23rd March 2016

DOI: 10.1039/c6ra01854h

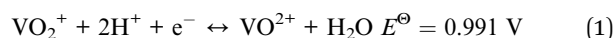
www.rsc.org/advances

1. Introduction

Microbial fuel cells (MFCs) are green energy devices that can convert organic or inorganic materials directly into electricity with the help of microorganisms as catalysts.^{1–3} Thus, the MFC has been considered as a promising sustainable technology to meet increasing energy demands due to its simultaneous wastewater treatment and electricity generation.^{4–6} In a typical MFC, electrons are produced in the anode chamber by catalysis of bacteria and then transferred to the cathode chamber through the external circuit where they are accepted by the electron acceptor.⁷ Previous studies indicate that oxygen is the most widely used electron acceptor for MFC cathodes, owing to its inexhaustible supply and low cost.⁸ However, the oxygen reduction reaction (ORR) needs an efficient catalyst to overcome the high overpotential during reaction.^{9,10} At present, platinum is commonly used as the ORR catalyst in MFCs, and the cost of precious Pt accounts for more than 50% of the cost of the whole MFC system.¹¹ Consequently, various modified catalysts have been developed with complicated fabrication processes.^{12,13} It is timely to explore cost-efficient approaches to improve MFCs' electricity recoveries with convenience.

Severe water pollution events result from the presence of high concentrations of vanadium that arise from vanadium mining and vanadium pentoxide production.¹⁴ Such events can lead to severe environmental damage.¹⁵ As a kind of

regenerative fuel cell, vanadium redox flow batteries (VRFB) stores relatively large scale amounts of energy by using V(v)/V(iv) and V(III)/V(II) redox couples in positive and negative cells,¹⁶ separated by a proton-conducting membrane.¹⁷ The equation of the vanadium redox couple reactions of V(v)/V(iv) is given below, with redox potential of 0.991 V.^{18,19}



Considering the excellent redox characteristics and abundant existence of vanadium(v) in metallurgical wastewater, it can be introduced in the cathode of MFCs for performance boost.

The present study demonstrated that the power outputs could indeed be enhanced by adding V(v) to the double-chamber air-cathode MFCs. Changes to the valence states of vanadium and its electrochemical behaviors were investigated. The results indicated that the addition of non-consumptive V(v) could be an effective means to enhance the power outputs of MFCs.

2. Materials and methods

2.1. Construction of MFCs and electrolyte conditions

Six double-chamber air-cathode MFCs were employed as previously described.^{20,21} All chambers were equipped with carbon fiber felt electrodes (4 cm × 4 cm × 1 cm) with total volume 250 mL for each chamber. The anode chambers were inoculated with 25 mL anaerobic sludge and filled with previously mentioned anolyte.^{20,21} The anode and cathode were connected by 100 Ω external resistances. The six MFCs were divided equally into three groups. The cathode chambers of two MFCs were filled with 250 mL phosphate buffer solution

^aSchool of Water Resources and Environment, China University of Geosciences Beijing, Key Laboratory of Groundwater Circulation and Evolution, Ministry of Education, Beijing 100083, China. E-mail: zbgcugb@gmail.com; baogangzhang@cugb.edu.cn; Fax: +86 10 8232 1081; Tel: +86 10 8232 2281

^bSchool of Engineering, The University of Edinburgh, The King's Buildings, Edinburgh EH9 3JL, UK

containing $V(v)$ of 150 mg L^{-1} , and oxygen was simultaneously introduced as bubbles by an inflator (MFC-VO). Another two MFCs were solely filled with 250 mL phosphate buffer solution containing $V(v)$ of 150 mg L^{-1} in the cathode chambers (MFC-V). The remaining two MFCs were solely aerated with 250 mL phosphate buffer as the catholyte (MFC-O).

2.2. Operations and analysis

After successful start-up and stable operation for three months, all the MFCs were filled with fresh analyte described above and operated in a 4 d fed-batch mode as most of organics was exhausted during this period. Electricity generation and the concentrations of $V(v)$ and $V(iv)$ were monitored. For each MFC, three cycles were carried out to check repeatability. All the experiments were conducted at room temperature ($22 \pm 2^\circ \text{C}$). The two MFCs in each group operated under the identical external conditions and the average results were recorded.

Chemical oxygen demand (COD) was measured by fast digestion spectrophotometric method (DR5000, HACH, USA). Concentrations of remaining $V(v)$ and generated $V(iv)$ were measured by spectrophotometric method.^{22,23} $V(III)$ and $V(II)$ were not monitored, given that they were rarely generated under this condition.²⁴ Total vanadium was detected by inductively coupled plasma mass spectroscopy. Voltages were recorded by a data acquisition system (PMD1208LS, Measurement Computing Corp., Norton, MA, USA) at 5 min intervals. Polarization curves were drawn with external resistances ranging from 5000 to 10Ω using a resistor box to evaluate the performance of the MFCs and the maximum power density. Coulombic efficiency (CE) was calculated as reported previously.²⁰ Cyclic voltammetry (CV) was performed at a scan rate of 0.01 V s^{-1} in the range of -0.6 V to $+0.8 \text{ V}$ using an electrochemical workstation (VMP3, Bio-Logic Science Instruments, France) with cathode

electrode and Ag/AgCl as working and reference electrodes, respectively.²⁵ Electrochemical impedance spectroscopy (EIS) measurements were carried out for the cathode of the MFCs over a frequency range of 100 kHz to 1 mHz with an AC signal of 10 mV amplitude.²⁶

3. Results and discussion

3.1. Evaluation of power outputs

After start-up, all the MFCs were fed with fresh electrolyte and their power outputs were recorded during three consecutive typical cycles (Fig. 1). The voltage outputs of MFC-O were slightly lower than those from previous studies using double chamber MFCs, due to the omission of catalysts, especially the absence of noble metal Pt.^{27,28} There were three main pathways for the oxygen reduction reaction (ORR) in the cathode of MFCs; a two-electron pathway (eqn (2) and (3)); a four-electron pathway as eqn (4); and a pathway comprising a mixture of the two- and four-electron pathways. The performance of MFCs was enhanced when ORR was accelerated with the aid of catalysts, following eqn (4). In the absence of catalysts, the two-electron pathway tended to develop, which was much slower than the four-electron pathway²⁹ thus reducing the performance of MFCs (Fig. 1). In fact, H_2O_2 was detected in the MFC-O with a maximum concentration of about 5.5 mg L^{-1} . The actual cathode potentials of MFC-O measured over the duration of the test ranged from $385.1 \pm 9.7 \text{ mV}$ to $115.7 \pm 13.2 \text{ mV}$, which was also consistent with other aerated cathode (both less than 400 mV).^{27,28}

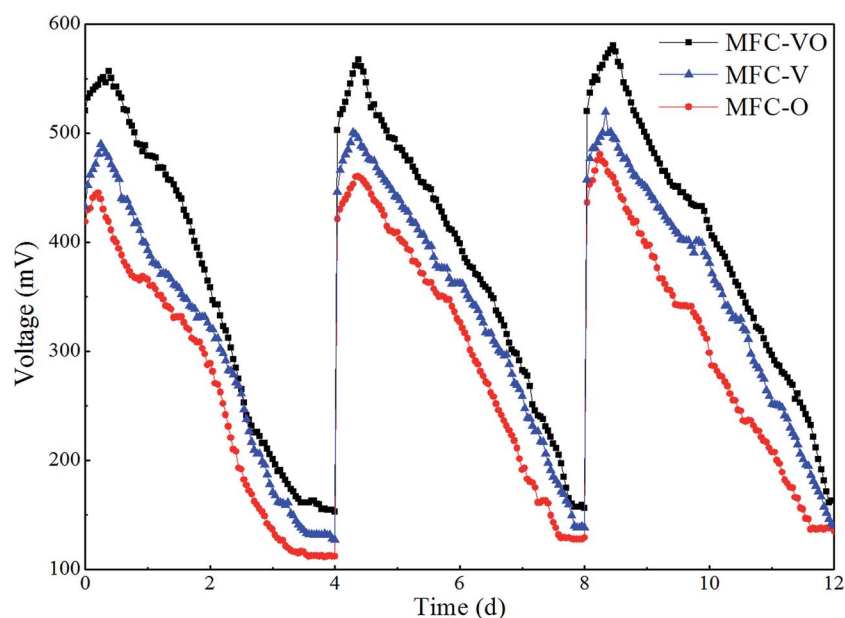
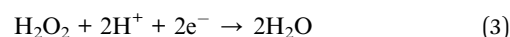
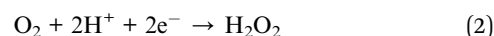


Fig. 1 The voltage outputs for MFC-VO, MFC-V, and MFC-O, with 100Ω external resistance during the three cycles operation.

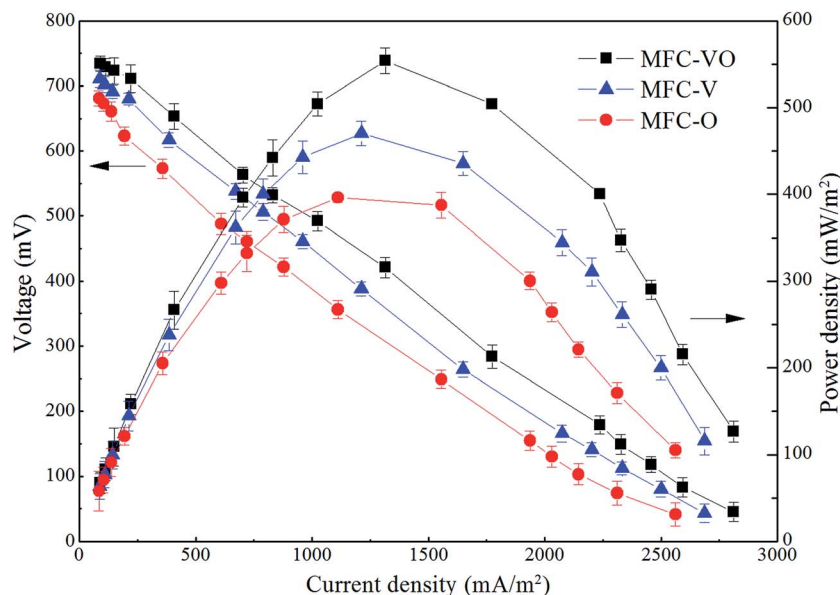
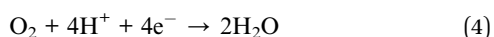


Fig. 2 Polarization curves and power outputs of the three groups of MFCs.



V(v) had the capacity to act as an alternative electron acceptor given its relatively higher electrode potential (eqn (1)), as indicated by MFC-V (Fig. 1) and our previous research.²⁴ Although the standard electrode potential of V(v) is lower than that of oxygen, it has larger solubility, and so the cathode potential could be improved (from 425.3 ± 7.4 mV to 125.9 ± 11.2 mV in a typical cycle) and the voltage outputs enhanced. By comparison, ORR is a gas phase reaction with large mass transfer resistance and much lower oxygen solubility;³⁰ hence, the voltage outputs of MFC-O were lower than those of MFC-V (Fig. 1).

Fig. 1 showed that the voltage outputs of MFC-VO were enhanced substantially with the increase of cathode potential in the presence of both V(v) and oxygen (from 498.4 ± 10.1 mV to 155.1 ± 18.5 mV during a typical cycle). Redox potentials of V(v) and oxygen based on Nernst equation were presented in eqn (5) and (6). Both V(v) and oxygen had relatively higher redox potentials, and were present together, leading to the higher voltage outputs of MFC-VO.

$$E_{\text{V}} = 991 + 59.21 \lg \frac{[\text{VO}_2^+][\text{H}^+]^2}{[\text{VO}^{2+}]} \quad (5)$$

$$E_{\text{O}} = 695 + 29.61 \lg \frac{[\text{O}_2][\text{H}^+]^2}{[\text{H}_2\text{O}_2]} \quad (6)$$

where $[\text{VO}^{2+}]$, $[\text{VO}_2^+]$ and $[\text{H}^+]$ are the concentrations of the different types of ions in solution. $[\text{H}_2\text{O}_2]$ is the concentration of H_2O_2 .

The power outputs of the three types of MFCs also exhibited similar behavior to those of voltage outputs, inferred from polarization curves (Fig. 2). MFC-VO achieved the highest

maximum power density of 553.9 mW m^{-2} with current density of 1315.6 mA m^{-2} , and the maximum power densities of MFC-V and MFC-O were representative.^{24,27,28} This was achieved due to the improvement in cathode potential with addition of V(v) in MFC-VO, confirming that addition of higher redox potential V(v) is a priming strategy to improve the power outputs of MFCs. Moreover, CEs of MFC-O and MFC-VO were 10.4% and 11.2%, respectively, both lower than that of MFC-V (16.9%), as oxygen could penetrate the proton exchange membrane and the generated electrons from organics oxidation could be consumed by oxygen instead of being transferred to anode.³¹

CV was used to evaluate the redox activities of cathode. The results are shown in Fig. 3 and it could be seen that MFC-VO had the largest closed-curve area, which was to say the electric quantity integrated by the closed curves was the biggest,

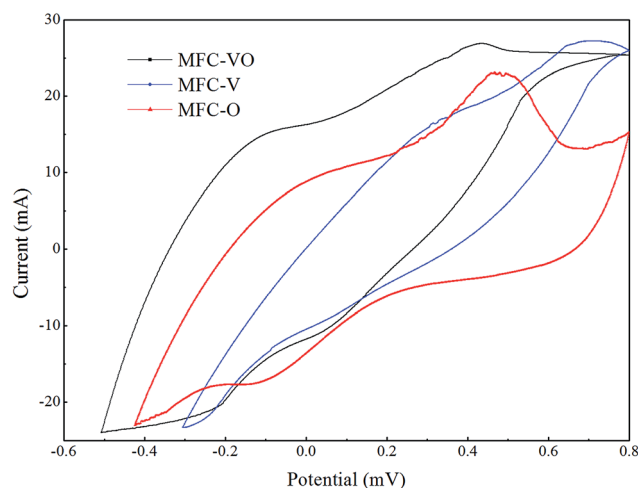


Fig. 3 CV curves of the three groups of MFCs.

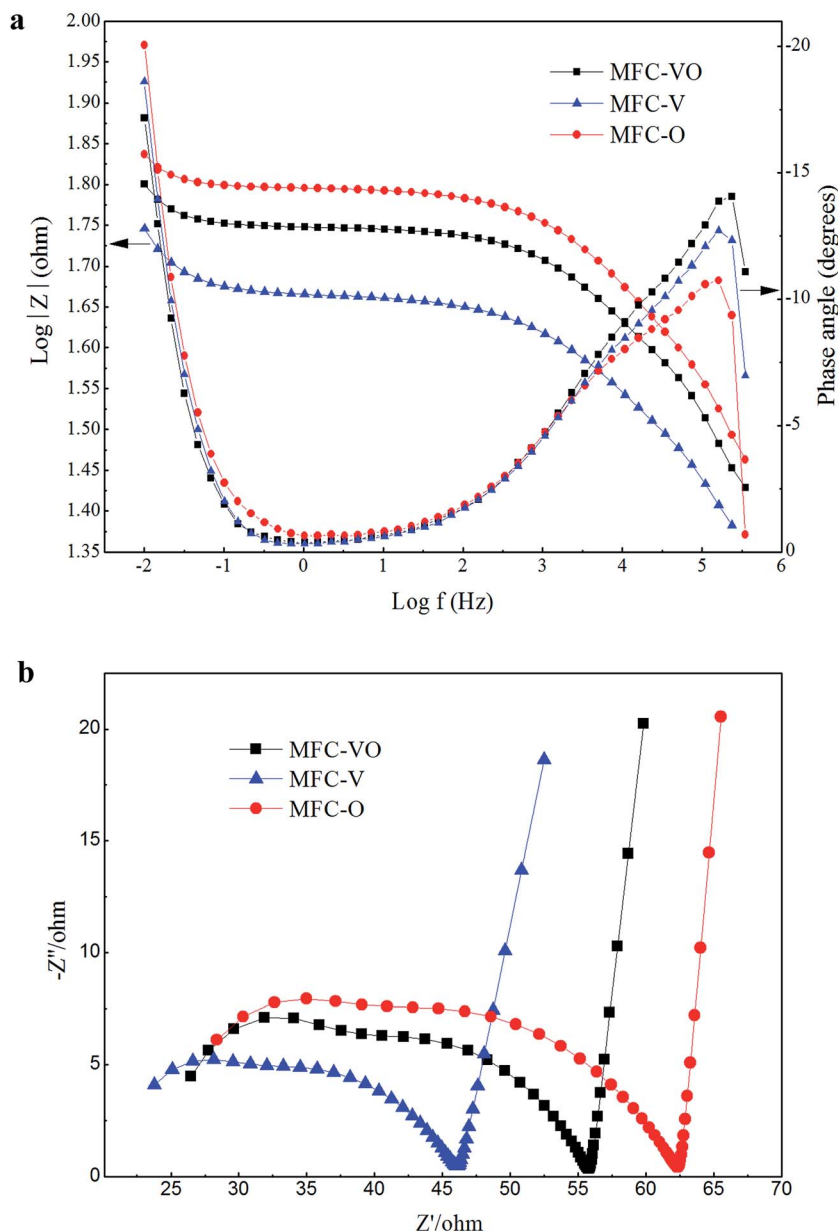


Fig. 4 EIS curves (a) and Nyquist plots (b) of the three groups of MFCs.

implying the highest electricity production.^{32,33} MFC-VO also exhibited an apparent reduction peak corresponding to positive current due to V(v) reduction, while the oxidation peak was slightly weak due to low concentration of generated V(IV) as well as the fast oxidation process by oxygen. Furthermore, the voltammogram for the catholyte containing V(v) indicated that the current flow was significantly higher in most potential regions than that for MFC-O. These results demonstrated that the addition of V(v) to the aqueous solution played an important role with respect to electron transfer in MFCs.

Fig. 4a showed the results obtained using EIS performed to evaluate the circuit resistance and kinetics for ORR in MFCs.^{34,35} It could be seen from the Fig. 4a that the modular curves show that maximum resistance was obtained for MFC-O, followed by

MFC-VO and MFC-V. This sequence occurred because the vanadium-containing solution had better conductivity than that with oxygen in the gas phase and the addition of vanadium reduced the cathode resistance. The EIS data were also analyzed using the one-time constant model³⁶ and the phase angles in the low-frequency region of the spectra indicated that the polarization resistance of the MFC-O was the highest due to the lack of catalyst for ORR.³⁷ Moreover, the Nyquist plots also confirmed these results and the calculated ohmic resistances for MFC-VO, MFC-V and MFC-O were 23.3 Ω , 20.2 Ω and 23.9 Ω , respectively (Fig. 4b). Additionally, monolayer reaction was observed in the MFC-VO as could be seen in the phase angle curves in Fig. 4a, implying that no solid vanadium chemicals were attached to the cathode surface which might hinder the

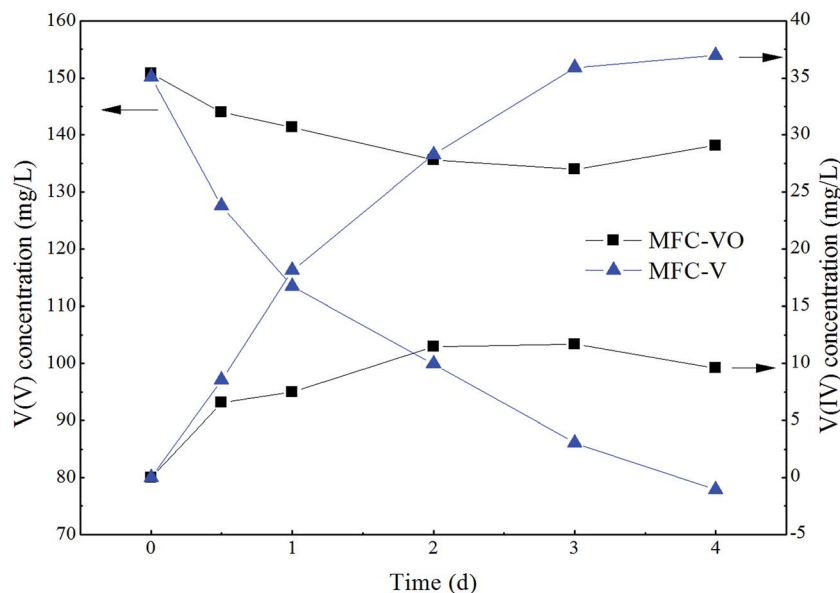


Fig. 5 Time histories of V(v) and V(iv) concentrations in the catholyte of MFC-VO and MFC-V during the 4 d operating period.

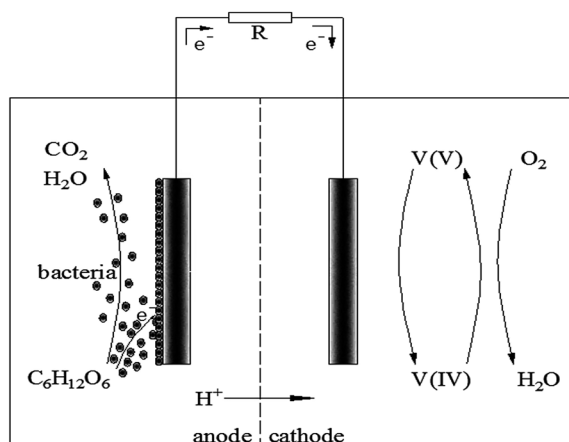


Fig. 6 Proposed pathways of MFC-VO improved by non-consumptive vanadium(v).

oxygen reduction reaction. This phenomenon differed from that of similar metal ions acting as electron acceptors in the cathode. For example, it was previously reported that Cr(vi) could also work as an alternative electron acceptor.^{38,39} However, Cr(vi), being an electron consumer, experienced great difficulty in undergoing *in situ* regeneration. Moreover, Cr(vi) reduced to Cr(III) with the latter attached on the cathode surface, which could affect the long-time operation of MFCs. In short, the addition of non-consumptive V(v) was more superior to enhance the performance of MFCs with long durability.

3.2. V(v) variations and mechanism studies

The concentration variations of V(v) and V(iv) in MFC-VO and MFC-V were monitored simultaneously throughout a typical cycle (Fig. 5). The concentration of V(v) decreased continuously and V(iv) was generated gradually in the MFC-V as V(v) was the

sole electron acceptor in the cathode chamber. Conversely, the concentration of V(v) in MFC-VO remained steady, and a much lower concentration of V(iv) was detected, indicating the non-consumption of V(v) in the proposed system. It should be mentioned that the initial concentration ratio of V(v) to oxygen was relatively higher to evaluate the function of V(v). When this value decreased, oxygen could be the electron acceptor and V(iv) would not be detected in the MFC-VO. The concentration of total vanadium kept relatively steady, indicated that precipitation reaction hardly happened in MFC-VO due to the introduced oxygen as it could oxidize the generated V(iv) easily.²⁰ Conversely, obvious precipitates appeared in MFC-V as the generated V(iv) is insoluble at neutral pH, resulting in the decrease of total vanadium in the catholyte.

Vanadium ion with higher redox potential acted as electron acceptor in the cathode chamber, as indicated in MFCs employing two different electron acceptors.⁴⁰ In the present study, V(v) took precedence of oxygen as it possessed higher redox potential, and so was reduced. Although it could improve the power outputs of MFCs, the electron-consuming V(v) would also increase costs and adversely affect the environment. When oxygen was simultaneously introduced, the generated V(iv) ions were further oxidized to V(v) quickly, realizing the regeneration of V(v) and avoiding the need for extra addition of V(v) during the operation. Oxygen was the terminal acceptor for electrons from anode. Fig. 6 showed the possible pathways for the entire process schematically.

Additionally, the effect of the change of conductivity with the addition of V(v) was also examined. When V(v) of 150 mg L⁻¹ was added to the phosphate buffer solution, a slight increase of conductivity was observed, from 4.98 mS cm⁻¹ to 5.44 mS cm⁻¹. For a test conducted with the same conductivity (5.44 mS cm⁻¹) adjusted by NaCl, hardly any increase in power output was measured. This provided further evidence that the enhanced power outputs were due to reaction of V(v) rather than increase

in conductivity. Meanwhile, these two species of vanadium were also measured in the anode chamber of MFC-VO with the same frequency as performed in the cathode chamber. Almost no V(v) or V(IV) ions were detected in the anode chamber and the total vanadium in the cathode chamber kept unchanged, indicating that vanadium ions were almost unable to penetrate the proton exchange membrane, thus preventing poisoning of microbes by toxic vanadium in the anode chamber and vanadium loss in the cathode chamber.

Moreover, other materials with higher redox potential could also be considered as candidates to improve MFC performance. Rhoads *et al.* used biomineralized manganese oxides as cathodic reactants, whereby MnO₂ was reduced to soluble Mn²⁺, and Mn²⁺ was then reoxidized with oxygen to manganese dioxide.⁴¹ However, this strengthening effect might be limited due to the reducing reaction of MnO₂ in the solid phase. The characteristics of their reduction products were also worth careful consideration; for example, chromium(vi) had previously been examined intensively in MFCs, but was found unsuitable to be employed in the aerated cathode because its reduction was insoluble Cr(III), which deposited on the cathode surface to block electrode reactions and was hardly oxidized again to Cr(vi) by oxygen.⁴² Moreover, the present research demonstrated similar benefits to a study of the use of Fe(III) to stimulate bioelectricity generation with regeneration of Fe(III) catalyzed by microbes, which required carbon sources as well as proper growth conditions.⁴³ However, the system proposed herein could function well with substantially less added chemicals and wider applicability to the environment. Wastewaters from vanadium mining and vanadium pentoxide production containing high concentration of V(v) could be directly employed as catholyte with oxygen being introduced in to improve the power outputs, while stopping aerating in the same system could realize the remediation of these wastewaters as indicated by MFC-V as well as our previous study.²⁰ In summary, the system proposed in the present research could generate higher bioelectricity without expensive catalysts, and without consumption of high redox potential materials, which were major advantages in the practical applications of MFCs.

4. Conclusions

After vanadium(v) (V(v)) was added to the catholyte, the power outputs of double-chamber air-cathode catalyst free MFCs reached as high as 553.9 mW m⁻². Cyclic voltammetry analysis and electrochemical impedance spectroscopy studies indicated the accelerated rate of electron transfer and a significant decrease of internal resistance with the addition of V(v). Moreover, the added V(v) was non-consumptive as it could be regenerated by aeration and residual V(IV) rarely attached to the cathode surface, a significant advantage over other multivalent ions that had been employed previously in MFCs with consumption and deposition. This study proposed a method of improving the performance of MFCs that had relative low costs and was simple to implement in practice.

Acknowledgements

This research work was supported by the National Natural Science Foundation of China (NSFC) (No. 21307117 and No. 41440025), the Research Fund for the Doctoral Program of Higher Education of China (No. 20120022120005), the Beijing Excellent Talent Training Project (No. 2013D009015000003), the Beijing Higher Education Young Elite Teacher Project (No. YETP0657) and the Fundamental Research Funds for the Central Universities (No. 2652015300, 2652015326).

References

- 1 X. Wang, Y. J. Feng, J. Liu, X. X. Shi, H. Lee, N. Li and N. Q. Ren, *Biosens. Bioelectron.*, 2010, **26**, 946–948.
- 2 V. M. Ortiz-Martínez, M. J. Salar-García, A. P. de los Ríos, F. J. Hernandez-Fernandez, J. A. Egea and U. Lozano, *Chem. Eng. J.*, 2015, **27**, 50–60.
- 3 A. Zabihallahpoor, M. Rahimnejad and F. Talebnia, *RSC Adv.*, 2015, **5**, 94171–94183.
- 4 S. Choi, *Biosens. Bioelectron.*, 2015, **69**, 8–25.
- 5 D. Pant, G. Van Bogaert, L. Diels and K. Vanbroekhoven, *Bioresour. Technol.*, 2010, **101**, 1533–1543.
- 6 W. L. Yang, H. X. Han, M. H. Zhou and J. Yang, *RSC Adv.*, 2015, **5**, 49513–49520.
- 7 Y. Yuan, B. Zhao, Y. Jeon, S. K. Zhong, S. G. Zhou and S. Kim, *Bioresour. Technol.*, 2011, **102**, 5849–5854.
- 8 Y. Yuan, J. Ahmed and S. Kim, *J. Power Sources*, 2011, **196**, 1103–1106.
- 9 B. Erable, D. Féron and A. Bergel, *ChemSusChem*, 2012, **5**, 975–987.
- 10 X. H. Tang, H. R. Li, W. D. Wang, Z. W. Du and H. Y. Ng, *RSC Adv.*, 2014, **4**, 12789–12794.
- 11 L. J. Zhang, X. J. Yin and S. F. Y. Li, *Chem. Eng. J.*, 2015, **276**, 185–192.
- 12 M. Ghasemi, W. R. W. Daud, M. Rahimnejad, M. Rezayi, A. Fatemi, Y. Jafari, M. R. Somalu and A. Manzour, *Int. J. Hydrogen Energy*, 2013, **38**, 9533–9540.
- 13 Z. F. Hu, C. Chen, H. Meng, R. H. Wang, P. K. Shen and H. G. Fu, *Electrochem. Commun.*, 2011, **13**, 763–765.
- 14 W. Carpentier, K. Sandra, I. De Smet, A. Brige, L. De Smet and J. Van Beeumen, *Appl. Environ. Microbiol.*, 2003, **69**, 3636–3639.
- 15 A. P. Yelton, K. H. Williams, J. Fournelle, K. C. Wrighton, K. M. Handley and J. F. Banfield, *Environ. Sci. Technol.*, 2013, **47**, 6500–6509.
- 16 F. Rahman and M. Skyllas-Kazacos, *J. Power Sources*, 2009, **189**, 1212–1219.
- 17 M. Vijayakumar, B. Schwenzer, S. Kim, Z. G. Yang, S. Thevuthasan, J. Liu, G. L. Graff and J. Z. Hu, *Solid State Nucl. Magn. Reson.*, 2012, **42**, 71–80.
- 18 M. Vijayakumar, M. S. Bhuvaneswari, P. Nachimuthu, B. Schwenzer, S. Kim, Z. G. Yang, J. Liu, G. L. Graff, S. Thevuthasan and J. Z. Hu, *J. Membr. Sci.*, 2011, **366**, 325–334.
- 19 K. L. Huang, X. G. Li, S. Q. Liu, N. Tan and L. Q. Chen, *Renewable Energy*, 2008, **33**, 186–192.

- 20 B. G. Zhang, H. Z. Zhao, C. H. Shi, S. G. Zhou and J. R. Ni, *J. Chem. Technol. Biotechnol.*, 2009, **84**, 1780–1786.
- 21 B. G. Zhang, S. G. Zhou, H. Z. Zhao, C. H. Shi, L. C. Kong, J. J. Sun, Y. Yang and J. R. Ni, *Bioprocess Biosyst. Eng.*, 2010, **33**, 187–194.
- 22 A. A. Ensafi, M. K. Amini and M. Mazloun-Ardakani, *Anal. Lett.*, 1999, **32**, 1927–1937.
- 23 A. Safavi, H. Abdollahi, F. Sedaghatpour and S. Zeinali, *Anal. Chim. Acta*, 2000, **409**, 275–282.
- 24 B. G. Zhang, C. X. Tian, Y. Liu, L. T. Hao, Y. Liu, C. P. Feng, Y. Q. Liu and Z. L. Wang, *Bioresour. Technol.*, 2015, **179**, 91–97.
- 25 R. Kakarla and B. Min, *Int. J. Hydrogen Energy*, 2014, **39**, 10275–10283.
- 26 S. J. You, Q. L. Zhao, J. N. Zhang, J. Q. Jiang, C. L. Wan, M. A. Du and S. Q. Zhao, *J. Power Sources*, 2007, **173**, 172–177.
- 27 A. Y. Cetinkaya, O. K. Ozdemir, E. O. Koroglu, A. Hasimoglu and B. Ozkaya, *Bioresour. Technol.*, 2015, **195**, 188–193.
- 28 Y. Y. Chang, H. Z. Zhao, C. Zhong and A. Xue, *Russ. J. Electrochem.*, 2014, **50**, 885–890.
- 29 Z. J. Wang, C. L. Cao, Y. Zheng, S. L. Chen and F. Zhao, *ChemElectroChem*, 2014, **1**, 1813–1821.
- 30 J. Z. Wang, B. G. Zhang, A. G. L. Borthwick, C. P. Feng and J. R. Ni, *Chem. Eng. J.*, 2015, **280**, 99–105.
- 31 B. G. Zhang, H. Z. Zhao, S. G. Zhou, C. H. Shi, C. Wang and J. R. Ni, *Bioresour. Technol.*, 2009, **100**, 5687–5693.
- 32 K. Ben Liew, W. R. W. Daud, M. Ghasemi, K. S. Loh, M. Ismail, S. S. Lim and J. X. Leong, *Int. J. Hydrogen Energy*, 2015, **40**, 11625–11632.
- 33 L. Z. Zeng, S. F. Zhao and W. S. Li, *Appl. Biochem. Biotechnol.*, 2015, **175**, 2637–2646.
- 34 G. Q. Li, L. G. Feng, J. F. Chang, B. Wichman, H. Gronbeck, C. P. Liu and W. Xing, *ChemSusChem*, 2014, **7**, 3374–3381.
- 35 A. Nandy, V. Kumar, M. Khamrai and P. P. Kundu, *RSC Adv.*, 2015, **5**, 41300–41306.
- 36 H. R. Ding, Y. Li, A. H. Lu, S. Jin, C. Quan, C. Q. Wang, X. Wang, C. P. Zeng and Y. Yan, *Bioresour. Technol.*, 2010, **101**, 3500–3505.
- 37 A. K. Manohar, O. Bretschger, K. H. Neelson and F. Mansfeld, *Bioelectrochemistry*, 2008, **72**, 149–154.
- 38 Y. Li, A. H. Lu, H. R. Ding, S. Jin, Y. H. Yan, C. Q. Wang, C. P. Zen and X. Wang, *Electrochem. Commun.*, 2009, **11**, 1496–1499.
- 39 C. Wang, H. Deng and F. Zhao, *Soil Sediment Contam.*, 2015, **25**, 1–12.
- 40 B. G. Zhang, C. P. Feng, J. R. Ni, J. Zhang and W. L. Huang, *J. Power Sources*, 2012, **204**, 34–39.
- 41 A. Rhoads, H. Beyenal and Z. Lewandowski, *Environ. Sci. Technol.*, 2005, **39**, 4666–4671.
- 42 Z. J. Li, X. W. Zhang and L. C. Lei, *Process Biochem.*, 2008, **43**, 1352–1358.
- 43 A. Ter Heijne, H. V. M. Hamelers, V. De Wilde, R. A. Rozendal and C. J. N. Buisman, *Environ. Sci. Technol.*, 2006, **40**, 5200–5205.